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OPTICAL PROPERTIES OF METALS



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UNIVERSITY OF CHICAGO

MARCH 1956

WRIGHT AIR DEVELOPMENT CENTER

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**WRIGHT AIR DEVELOPMENT CENTER
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UNITED STATES AIR FORCE
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FOREWORD

The research described in this report was conducted at the Institute for the Study of Metals of the University of Chicago in fulfillment of Contracts AF 33(038)-6534 and AF 33(616)-2090 with the Air Research and Development Command, United State Air Force. These contracts extended from 1950 to 1955 and were administered by the Chemistry Research Branch, Aeronautical Research Laboratory of the Wright Air Development Center.

This report, in conjunction with WADC TR 55-70, is a comprehensive summary of the portion of the research conducted by Professor L. G. Schulz.

Publications in the learned journals arising from the research reported herein include:

- "An Interferometric Method for Accurate Thickness Measurements of Thin Evaporated Films", (J. Opt. Soc. Am. 40 (1950), p. 690).
- "An Experimental Study of the Change in Phase Accompanying Reflection of Light from Evaloprated Films", (J. Opt. Soc. Am. 40 (1950), p. 760).
- "The Effect of Phase Changes in White Light Interferometry", (J. Opt. Soc. Am. 41 (1951), p. 261).
- "An Interferometric Method for the Determination of the Absorption Coefficients of Metals, with Results for Silver and Aluminum", (J. Opt. Soc. Am. 41 (1951), p. 1047).
- "The Optical Constants of Silver, Gold, Copper, and Aluminum. I. The Absorption Coefficient k ", (J. Opt. Soc. Am. 44 (1954), p. 357).
- "Optical Constants of Silver, Gold, Copper, and Aluminum. II. The Index of Refraction n ", (J. Opt. Soc. Am. 44 (1954), p. 362).
- "An Experimental Confirmation of the Drude Free Electron Theory of the Optical Properties of Metals for Silver, Gold, and Copper in the Near Infrared", (J. Opt. Soc. Am. 44 (1954), p. 1540).

This work was carried out as Task 70320, Project 7351, "Surface Reaction in Metals," with Dr. L. A. Wood as task scientist for Wright Air Development Center.

ABSTRACT

The optical properties of Ag, Au, and Cu were studied experimentally and the results compared with those predicted by the Drude free electron theory. It was found that beyond about two microns the experimental results are in good agreement with the Drude theory. To bring about this agreement it was necessary to use the effective mass of the electrons in a metal as an adjustable parameter. Comparison of the results of reflection and transmission experiments suggested the existence of special surface properties of metals.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



ALDO LINGARD, Colonel, USAF
Chief, Aeronautical Research Laboratory
Directorate of Research

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OPTICAL PROPERTIES OF METALS

I. INTRODUCTION.

The experimental work described in this report was undertaken to determine to what extent optical methods can be used to test various theories of metals, in particular the original free electron theory of Drude. Unlike most current research dealing with the optical properties of metals, it is not concerned with semiconductors such as germanium, but with "good" monovalent metals such as Ag, Au, and Cu. The earliest papers concerned with these materials date back to before 1900. Unfortunately most of early work is not reliable because of the difficulty at that time in preparing suitable samples on which to make the optical measurements.

At the present time the experimentalist working in this field has two great advantages.

1. Ideally clean samples can be prepared by evaporation and condensation in a vacuum.¹
2. Excellent commercially built infrared equipment is now available.²

Moreover, there have been recent advances in the theory which help to explain certain puzzling features of the experimental results.³ For some time experiments had been in progress which used optical methods for making film thickness measurements.⁴⁻⁷ The techniques developed for that purpose proved to be very useful in devising new procedures for the study of the optical properties of metals. These techniques will be referred to at the appropriate place in the record of results.

NOTE: This Technical Report was released by the author for publication in December 1954.

Since the field being considered is not a popular one, the next five sections (II to VI inclusive) will review some of the standard but often forgotten optical theory. The experimental results of the new work^{8,9,10} on Ag, Au, and Cu will follow. Because the work is still in progress on other metals a final statement cannot be made at this time.

II. ELECTROMAGNETIC WAVES IN METALS

Assume that we have an interface of a dielectric with index n_0 and a metal such as silver. Any light which might be incident from the dielectric side will be largely reflected; a smaller part passes through the interface into the interior of the metal where it is absorbed and changed to heat. Within the metal, propagation is still by a wave motion, accordingly, we can write the equation

$$E_t = E_s \exp - \frac{2 \pi i n t}{\lambda} \exp - \frac{2 \pi k t}{\lambda} \quad (1)$$

In this equation E_t is the electric vector at any depth t where E_s is its value at the surface. The first exponential with the imaginary exponent is identical with the term for propagation of light in a dielectric, but for metals there is an additional term, another exponential with a real exponent. It describes the rate at which the amplitude is damped out as a consequence of absorption. λ as usual is the wavelength of the radiation in a vacuum. Of interest for this discussion are the two constants n and k . n is the index of refraction, that is the ratio of the phase velocity in a vacuum to that in the metal. k has been given various names. Most

properly it is simply a damping factor, but following common practice, it will here be called the absorption coefficient although absorption is actually given by the product nk rather than to k alone. Another expression commonly used is the complex index of refraction defined in this manner:

$$\bar{n} = n - ik. \quad (2)$$

Classical optical theory principally the work of Fresnel,¹¹ has provided us many relations between n and k and more directly measurable quantities. For example, returning to reflectivity, the intensity of the reflected light relative to that which is incident, depends both on n and k in the following way:

$$R = \frac{(n - n_0)^2 + k^2}{(n + n_0)^2 + k^2} \quad (3)$$

In describing reflection there is also a phase change to be defined. It is given by this equation:

$$\tan \psi = \frac{2k n_0}{k^2 + n^2 - n_0^2} \quad (4)$$

Eqs. (1) and (2) are for normal incidence. Electromagnetic theory has provided equations for the general case of oblique incidence, but they are usually too complex to be useful. Rather than give any of these for the reflectivity, it is easier to illustrate the angular dependence for a representative case such as that given in Fig. 1. Here R_s is the reflectivity in the s plane; R_p that for the p plane. R_s rises continuously but R_p drops, passes through a minimum, and then rises to unity. At 45 degrees there is a simple relation between R_s and R_p :

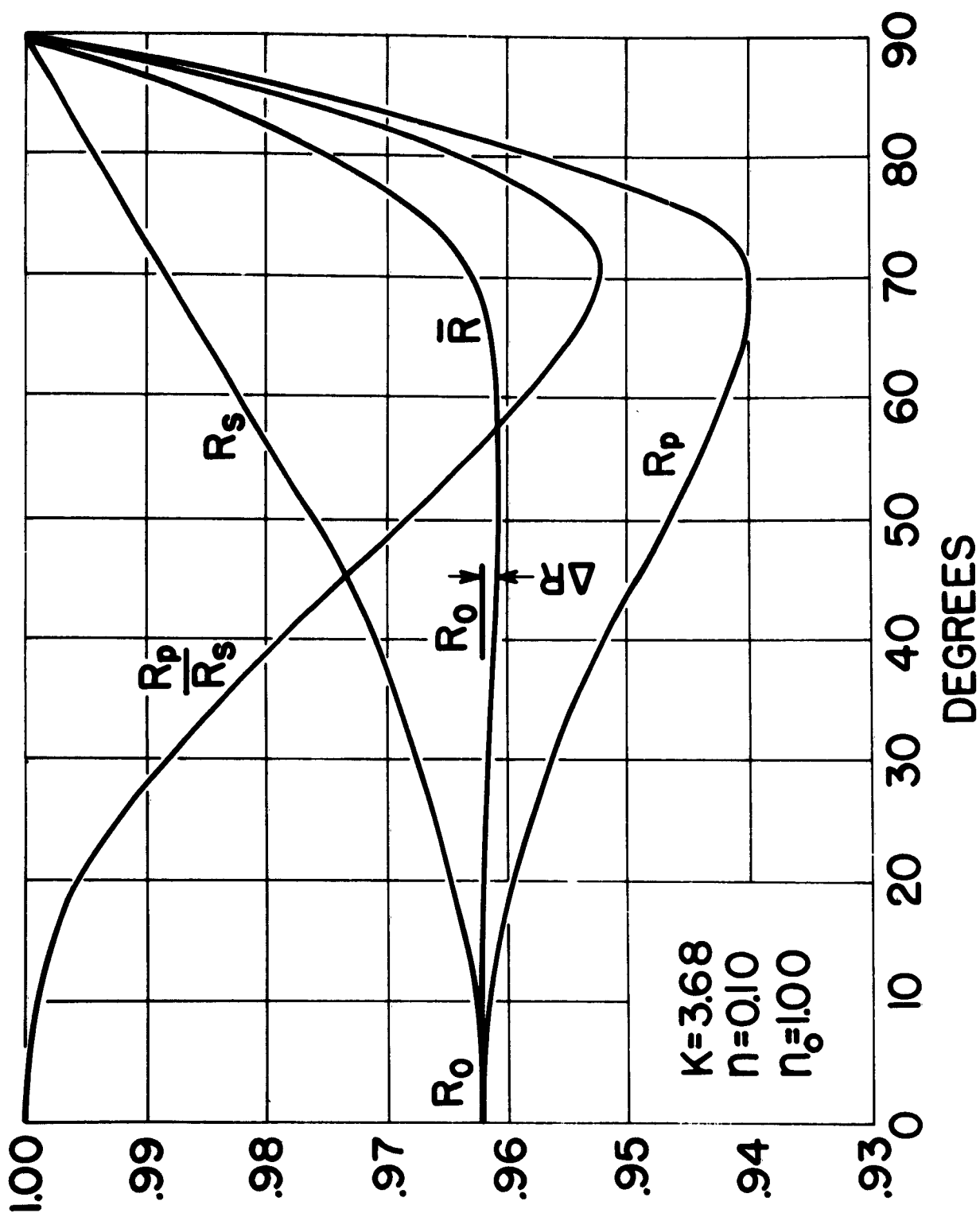


Figure 1. Reflectivities for Changing Angles.

$$R_p = R_s^2 \quad (5)$$

The graph shows that at grazing incidence all materials become totally reflecting, as indeed is shown by common experience.

Leaving reflectivity, suppose the metal is reduced to say the order of 500A in thickness. A small but appreciable amount of radiation is then transmitted. The actual amount is a function of n and k as shown in Eq. (6) and (7) for the case of normal incidence.

$$\text{where} \quad T = Ce^{-4\pi kt/\lambda} \quad (6)$$

$$C = \frac{16n_1n_3(n_2+k)^2}{[(n_2+n_1)^2+k^2] [n_2+n_3)^2+k^2]} \quad (7)$$

Here n_1 refers to the dielectric (air) in front of the metal, n_3 to the glass support of the metal, and n_2 and k to the metal itself. (Eqs. (6) and (7) will be discussed further in connection with Figs. 9 and 10)

These equations and others like them define in a practical way what is meant by the optical constants of metals. Suppose now that one is faced with the problem of determining n and k experimentally. This amounts to selecting a pair of the equations that suggest two reasonable experiments; always a pair because there are two unknowns, n and k . Electricity books are more complete than optics texts -- Stratton,¹² for example. The difficulty is to gain a feeling for the relative magnitudes in the optical case. In connection with reflectivity, Stratton considers radio waves on sea water which in principle is identical with the optical case but

requires a radically different experimental approach.

III. OPTICS AS A BRANCH OF ELECTRICITY.

From a general point of view optics deals with high frequency electricity. Admittedly, there is a big gap at the moment between what is customarily taken as the infrared limit and the highest frequency micro waves. But, nevertheless, n and k are in a sense electrical as well as optical constants. If they are, it should be possible to relate them to the usual electrical parameters such as conductivity σ and electron density N ; thus,

$$n, k = F(\sigma, N, \dots) \quad (8)$$

This relationship is, of course, reversible, but should go from the better known to the less known. It seems that theories of conductivity have gone as far as present ideas permit, therefore it might be more profitable to give some attention to the optical or high frequency side of the relationship. From this point of view the several fields are related: optics, electricity, and solids. Since the experimental techniques employed here are those traditionally known as optical, the work here presented will be called experiment on the optical properties of metals.

IV. ABSORPTION OF RADIATION BY SOLID MATTER

Before going into the details of theory or experiments, it is worth while indicating roughly the extent of our knowledge concerning the interaction of radiation and solid metals. The sketch of the

E. M. SPECTRUM

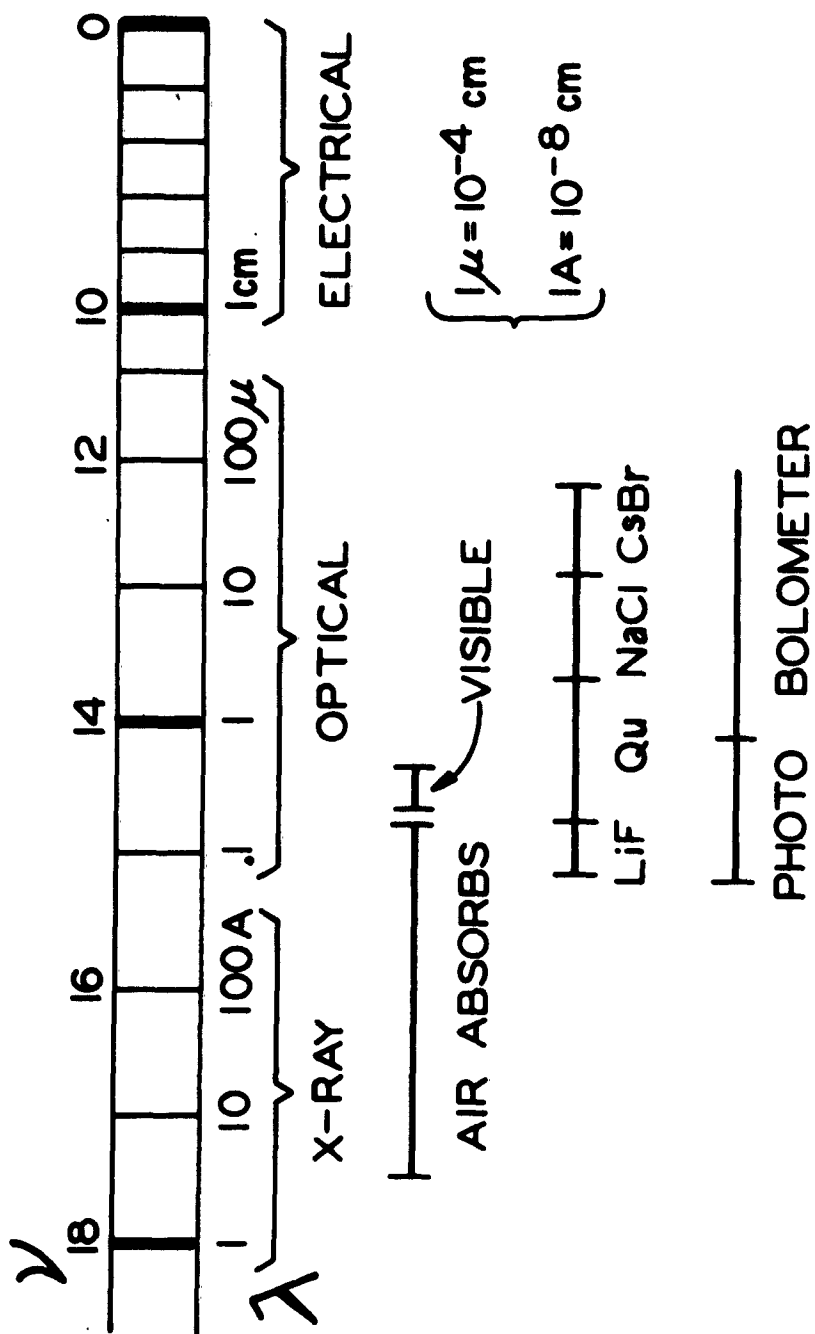


Figure 2. Electromagnetic Spectrum.

electromagnetic spectrum given in Fig. 2 will aid in making a quick survey. Along the top from right to left is shown the frequency in powers of 10. Below, from left to right is given the associated wavelength, λ , using units commonly employed. In the X-ray region of high frequency and short wavelength, the properties of matter are independent of the physical state, that is, X-rays are characteristic of atoms and not the state of aggregation. However, as the wavelength is increased to about 100A, the upper lying energy levels of an atom in a solid are altered. So-called soft X-rays can be used to investigate the density of these levels at least, for alkali metals. Several years ago this procedure was considered a very promising approach to the study of solids but the optimism and enthusiasm has now died away. The experimental as well as the theoretical difficulties are apparently very great.

In the middle of spectrum the more restricted optical range, there was great interest about 1890 to 1915. Drude led the way by developing his free electron theory of metals and also devising experiments. In spite of a long period of experimental work, some of it continuing until the present time, no clear-cut conclusions were reached concerning the validity of the theory. It is now generally agreed that the experimental work has not been reliable because of defects in the samples on which the optical measurements were made.

Continuing now to the very long wavelengths, 1cm and longer, we come into a region in which optical phenomena has been understood since the time of Faraday. In fact, the classical skin effect is part of standard electrical engineering knowledge.

Looking at the whole situation, the extremes are best understood; atomic properties and low frequency electricity. Efforts have been made to advance from the left, that is, with soft X-rays. It seemed worth while to try another approach: from the skin effect region into the infrared. There have been some brave but not very cautious individuals who have explored the middle region, but at best they have built up little islands of information unrelated to the facts at the ends.

A few items of practical interest are included in Fig. 2 for orientation purposes: the visible region is 0.4μ to 0.7μ . Quartz transmits from about 0.2μ to 3μ where NaCl is used to extend the range to 12μ ; CsBr will go somewhat farther. Below quartz, LiF optics can be used, which is trouble enough, but in addition air is absorbing here, and then too there is really no satisfactory light source. The standard detectors are photographic materials and bolometers of the kind used in the infrared. Commonly used units of length are defined in the lower right.

V. THE DRUDE FREE ELECTRON THEORY OF SOLIDS

Theories relating the observed optical and the assumed electrical properties of solids were developed at an early date. The dispersion of dielectrics is a convenient point to start the general theory. About 1800 Lorentz explained absorption in dielectrics by assuming bound charges which become polarized by the passing light wave. Eq. 9 is the usual one for forced oscillations:

$$m\ddot{y} + 2\pi m\dot{y} + Ky = -eE \exp 2\pi i\nu t \quad (9)$$

m is the mass of the oscillator; gamma is a damping factor, and K is an elastic constant. A theory based on the physical ideas associated with this equation was able to explain the observed optical properties of most insulators. The contribution of Drude was to assume free rather than bound charges. The elastic constant K in eq. 9 was taken equal to zero, accordingly the last term on the left dropped out giving,

$$m\ddot{y} + 2\pi m\gamma\dot{y} = -eE \exp 2\pi i\nu t \quad (10)$$

For completeness and to show the relationship of the various theories Eq. 11 is given for the case of the classical skin effect:

$$2\pi m\gamma\dot{y} = -eE \exp 2\pi i\nu t \quad (11)$$

At low frequencies the inertial reaction $m\ddot{y}$ of the charge is small relative to resistance damping, $2\pi m\gamma\dot{y}$, therefore only one term remains on the left.

Returning to the Eq. 10, it was postulated that a metal contains "free" electrons which interact with the electromagnetic field of the passing light wave. Nothing more was said explicitly concerning mean free path or collision frequency. Taking this one idea of free electrons, Drude was able to work out a theory of metals which included a relationship between n and k and the properties of free electrons. Since the algebraic steps are given in various texts,^{13,14} We shall pass on directly to the working equations:

$$n^2 - k^2 = 1 - 2 \left(\frac{Ne^2}{2\pi m^*} \right) \left(\frac{1}{\gamma^2 + \nu^2} \right) \quad (12)$$

$$nk = \frac{\gamma}{\delta} \frac{Ne^2}{2\pi m^*} \frac{1}{\delta^2 + \gamma^2} \quad (13)$$

where

$$\gamma = \frac{Ne^2}{2\pi m^*} \frac{1}{\sigma} \quad (14)$$

In the expressions to the right, N is the number of electrons per unit volume, m^* is their effective mass, and ν (μ) the frequency of the radiation involved. Gamma (γ) is also a frequency characteristic of the metal, and inversely proportional to the direct current conductivity sigma (σ).

Again, for comparison, the equations of the classical skin effect are included:

$$n = k \approx \sqrt{\sigma \lambda} \quad (15)$$

Here n and k are equal, and each is proportional to the square root of the conductivity. The electron mass or density does not appear.

In using the Drude equations it is common practice to assume that the number of free electrons per atom is equal to the chemical valence. For a monovalent metal such as Ag, the electron and atomic density are equal. Lacking other information, the effective mass is taken equal to the free mass. The equations become more meaningful after numbers are put in; Fig. 3 shows the dispersion of n and k for the case of Ag. In the long wavelength region where n and k are equal, both the curves unite with that given by skin effect theory. In a rough way one might think of the k/λ curve as measuring the inertial reaction of the electrons and n/λ measuring the electrical resistance. Around 1μ , where $n \ll k$, the first of Drude's equations

OPTICAL CONSTANTS OF SILVER

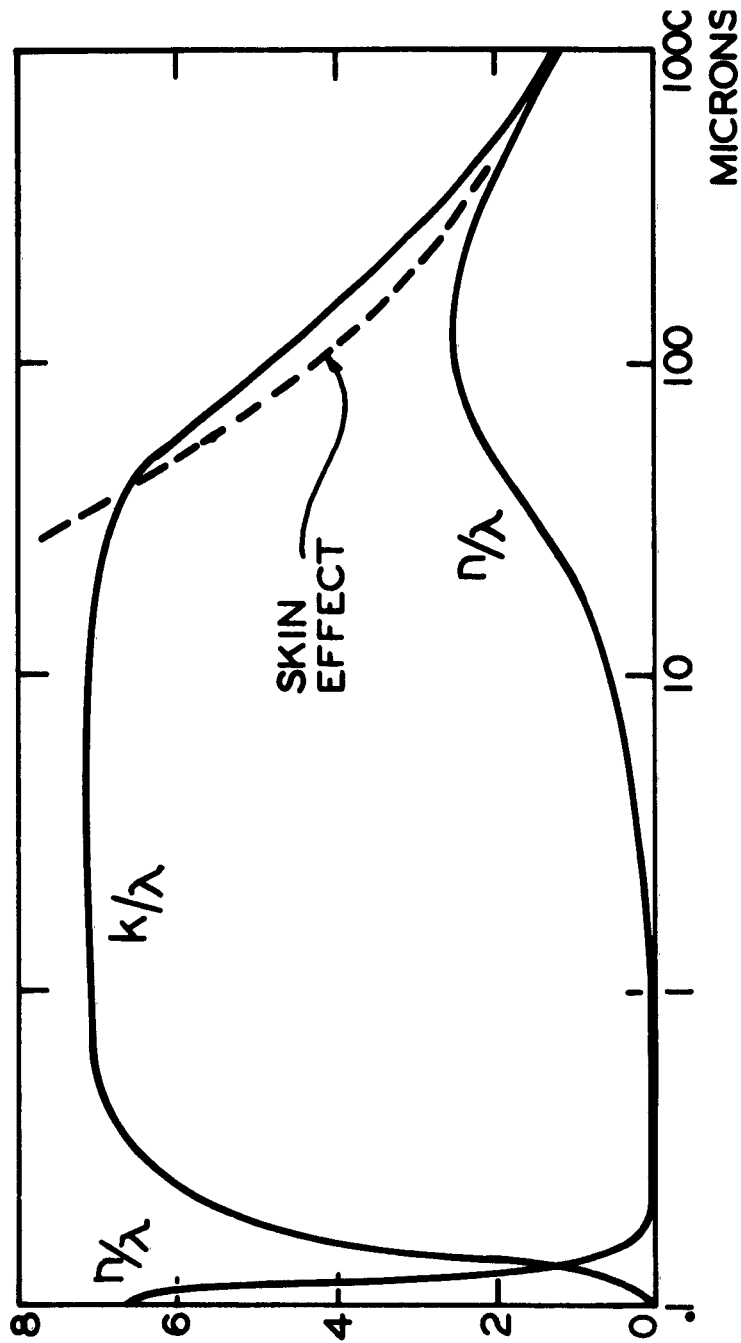


Figure 3. n/λ and k/λ for Ag.

reduced to a form which says that k/λ is a constant and independent of λ or conductivity. The experimental value of k/λ makes possible a determination of m^* , the effective mass of an electron in a metal lattice.

Attention to the absolute values on the graph will help to emphasize some of the experimental difficulties to be overcome. First, there is very small dispersion or variation with wavelength in either curve. The only sharp change occurs in the ultra violet. With the exception of the alkali metals, this region is inaccessible, however. It is therefore necessary to measure intensities, which means photometry, usually a more difficult procedure. Even more so because the reflectivity is around 99½% or above. Secondly, an enormous wavelength range must be explored, thus requiring measurements in the ultra violet, visible, and infrared. Third, the extremely high value of k/λ means that in practice for metals like silver the intensity of the radiation that gets through the surface has dropped to about 1% in a few hundred angstroms. If transmission experiments are done, thickness of this order must be measured with great accuracy. A fourth problem is that of preparing samples. Until recently this was done by metallurgical procedures which left the metal in an abnormal form as shown by the difference of the results from recently made measurements done on evaporated films.

The curves given in Fig. 3 are calculated values. The early experimental work was all in the visible or ultra violet where the Drude equations are not likely to apply. Enough cases of approximate agreement have been found, however, to show that the theory may be essentially correct. For example, the alkali metals in the ultra-violet and most liquid metals in the visible. But on the whole

the agreement of theory and experiment has been very poor.

VI. SURFACE EFFECTS

Any theory of solids, including Drude's theory, deals with the interior but of necessity an optical experiment involves reflection of radiation. Therefore surface as well as bulk properties are involved. The main physical idea is that the electron paths are shortened by collision with the surface. Since resistance is proportional to the collision frequency, the conduction must drop as one approaches the surface, leading to an increase in the effective value of the index of refraction.

There is also a change in the value of k but it is more difficult to show by a descriptive argument. The experimental value obtained by a surface measurement will be low. On the other hand, in a transmission experiment where the sample is at least somewhat thicker than the classical skin depth, the experimental value of k will approximate that for the bulk value.

In addition to these surface effects which are common to direct currents as well as to the high frequencies associated with light waves, there is a more basic deviation from Drude's theory. The phenomena associated with this deviation have become known as the "anomalous skin effect" and is the work primarily of Sondheimer³, Dingle¹⁵, and Holstein¹⁶.

VII. SUMMARY OF THE EXPERIMENTAL RESULTS

The general plan in this work was to use the Drude theory as a guide to the selection of experiments. Then, after suitable experimental techniques had been developed, the measurements were confined to the most promising metals. The principal results are here summarized:

1. Confining the work to Ag, Au, and Cu in the region of 1 to 3 microns, it was found that n and k had the proper wavelength dependence, but to obtain numerical agreement m^* (the effective mass) was used as an adjustable parameter.
2. Special surface effects were observed for both n and k measurements.
3. In addition the experiments also lead to a new set of values for the effective mass of electrons in Ag, Au, and Cu.

In the following sections experimental details will be shown, and procedures described by which these general conclusions were reached. Most of the effort was directed into experimental measurements in the infrared¹⁰ but some work was also done in the visible region.^{8,9}

VIII. MEASUREMENT OF THE INTENSITY OF REFLECTION (See references # 9 and # 10)

To avoid corrosion and general contamination from the air, measurements were made at glass-metal and quartz-metal interfaces. Four right angle prisms were arranged in the manner shown in Fig. 4. A ray of light incident normally from the left after four internal reflection leaves the opposite face unchanged in direction and without displacement. One-half of each hypotenuse face was covered

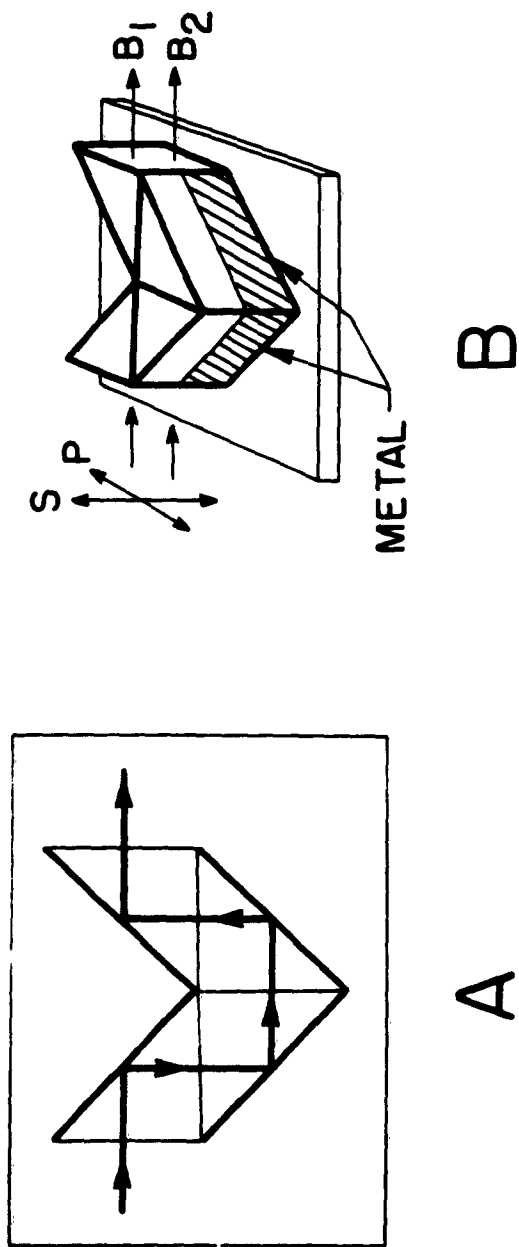


Figure 4. Reflectivity Samples.

with a film of the metal being studied. A ray through the upper half of such a sample was totally reflected at glass-air interfaces. Thus beam B_1 could be used as a reference against which to compare B_2 which was reflected at glass-metal interfaces. A necessary condition required for the legitimate applications of the equations of electromagnetic theory is that at 45 degrees R_p is equal to R_s^2 . To within the experimental accuracy this condition was always satisfied.

All equations of classical optics such as those mentioned earlier, Eqs. 1-7 assume that the interface of the metal with the neighboring dielectric is a plane surface, and moreover it is assumed that the optical properties change discontinuously at the boundary. In practice a surface is sufficiently smooth when the roughness amplitude is small in relation to the wavelength of the light, let us say one one hundredth of a wavelength. Such smoothness can be obtained at a glass-metal interface, but not the free surface of a metal in contact with air. The second assumption concerning a discontinuous change at the interface is usually harder to handle, and it was for this reason that the right-angle prism method was first tried. If any sort of gradient had existed, the relation $R_p = R_s^2$ would not have been satisfied.

Following the deposition of the metal by an evaporation procedure, the prisms were kept in a vacuum annealing furnace for a few days. The maximum temperature for metals of the kind Ag, Au, and Cu was about 120 degrees C. Higher temperatures caused a change that upset this relation of R_s to R_p . The purpose of annealing was to remove the strains and crystal defects of every kind that are

invariably produced in the condensation process. Aging at room temperature was also effective, but it required about a year to go to completion.

In the visible region measurements were made with a Beckman¹⁷ spectrophotometer and the complete equations of Fresnel then used to calculate the indices of refraction n . Since there is no particular interest in the reflectivities at glass-metal interfaces measured at an angle of 45° , only then values calculated from such measurements will be given. Table I lists the n values obtain over a range of wavelengths and Fig. 5 shows the same information graphically.

In the infrared region the interest was not so much in the determination of the value of n , but in checking the prediction of the Drude theory. Still using the samples of the type shown in Fig. 4 the index n was determined, and the reflectivity calculated for the case of normal incidence on a metal-air interface. For comparison several values of the reflectivity R are shown in Fig. 6. Beginning with the bottom, curve HR indicates the results of Hagen and Rubens.¹⁸ The short line at 0.993 labelled 1953 shows the new results with the four-prism type sample. Finally, the upper curve at 0.996 is the calculated reflectivity based on the Drude free electron theory. Since the absorption is measured from unity downward this difference 0.003 between the two uppermost curves, is a big error. Even with persistent effort, however, samples with reflectivity higher than 0.993 could not be produced. The deficiency of 0.003 is, however, just that predicted from special surface effects.¹⁶

TABLE I. Values of the index of refraction n for
Ag, Au, Cu, and Al.

(μ)	Ag	Au	Cu	Al
0.40	0.075	1.45	0.85	0.40
0.45	0.055	1.40	0.87	0.49
0.50	0.050	0.84	0.88	0.62
0.55	0.055	0.34	0.72	0.76
0.60	0.060	0.23	0.17	0.97
0.65	0.070	0.19	0.13	1.24
0.70	0.075	0.17	0.12	1.55
0.75	0.080	0.16	0.12	1.80
0.80	0.090	0.16	0.12	1.99
0.85	0.100	0.17	0.12	2.08
0.90	0.105	0.18	0.13	1.96
0.95	0.110	0.19	0.13	1.75

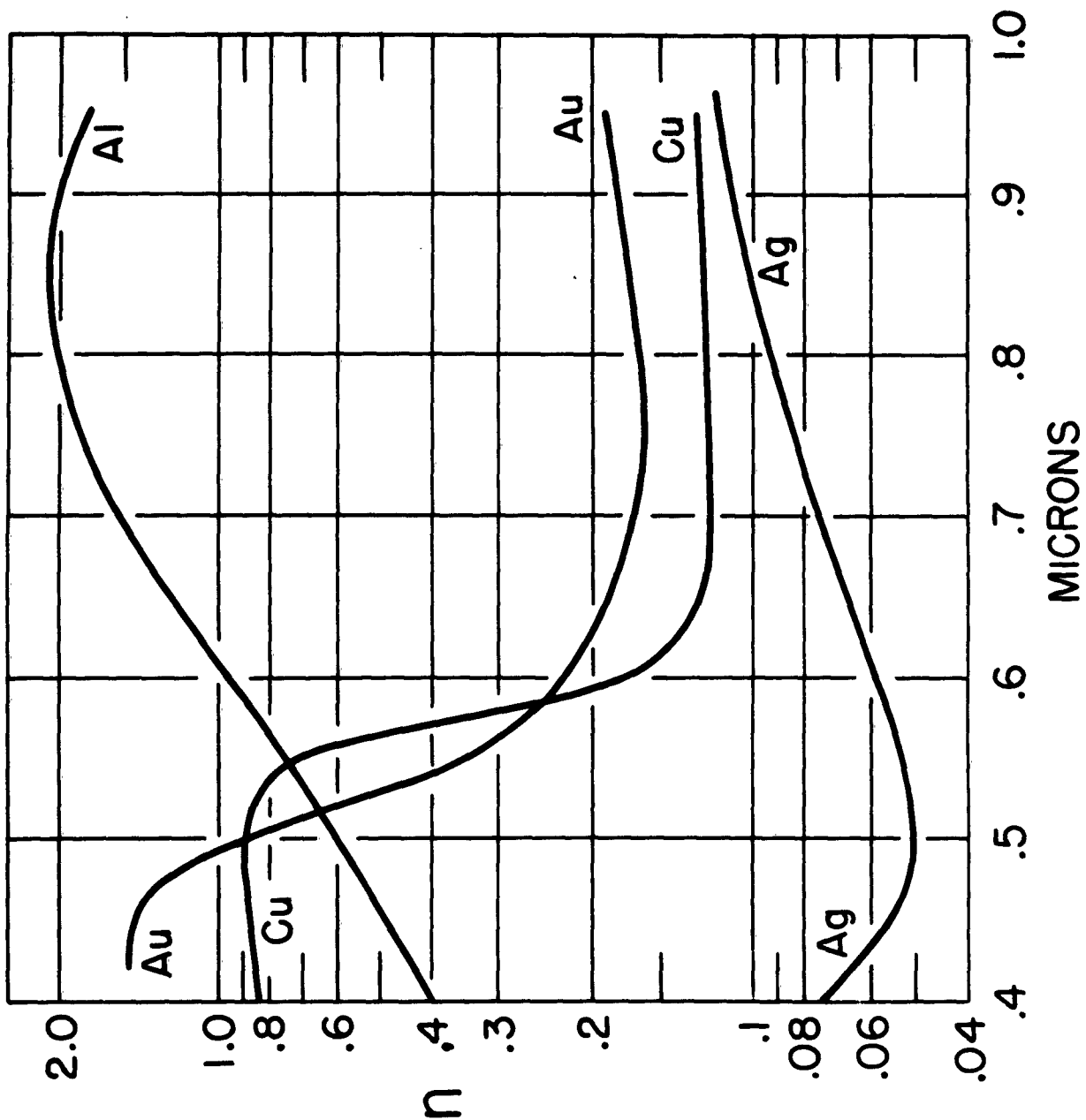


Figure 5. Values of n for Ag, Au and Cu.

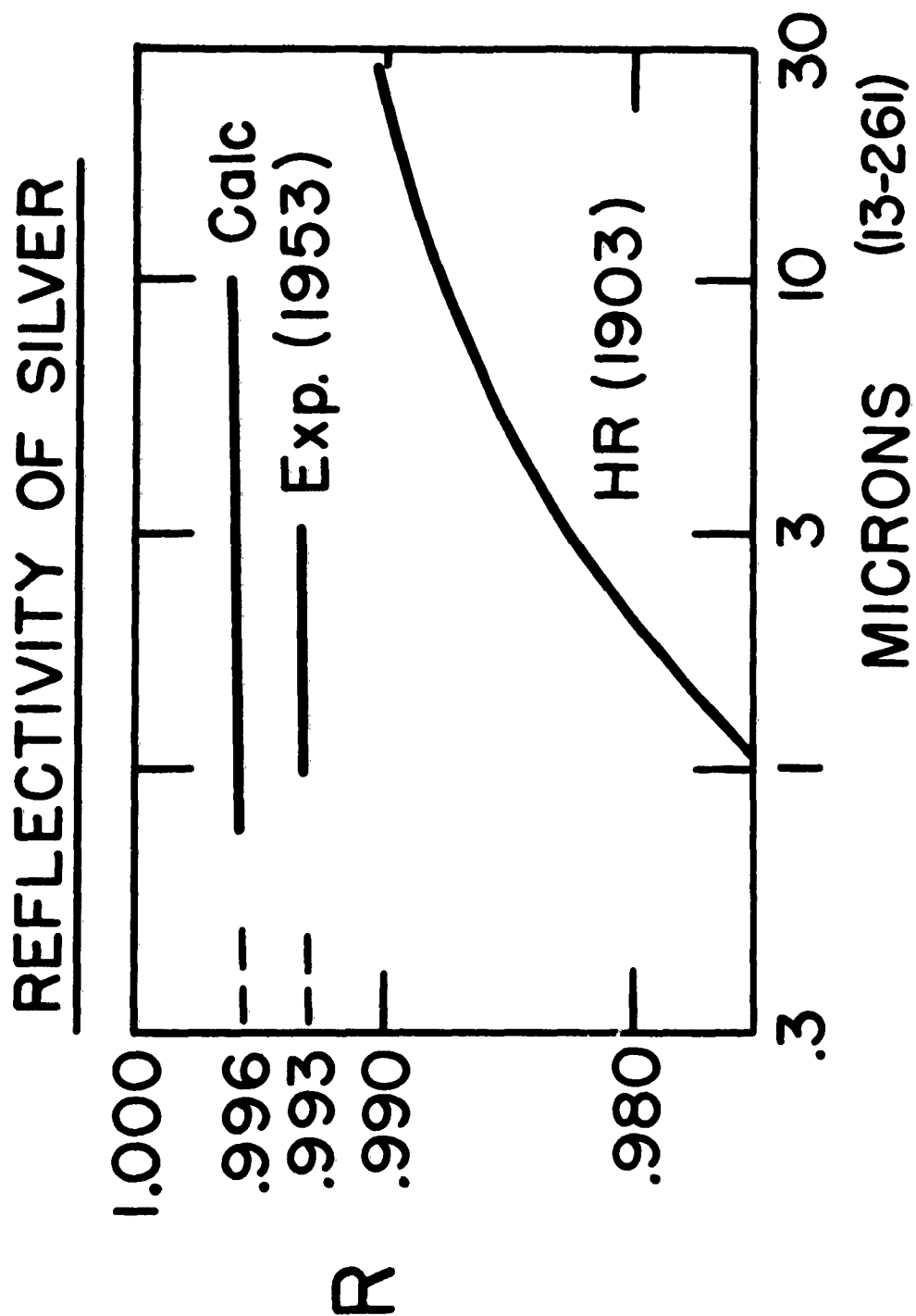


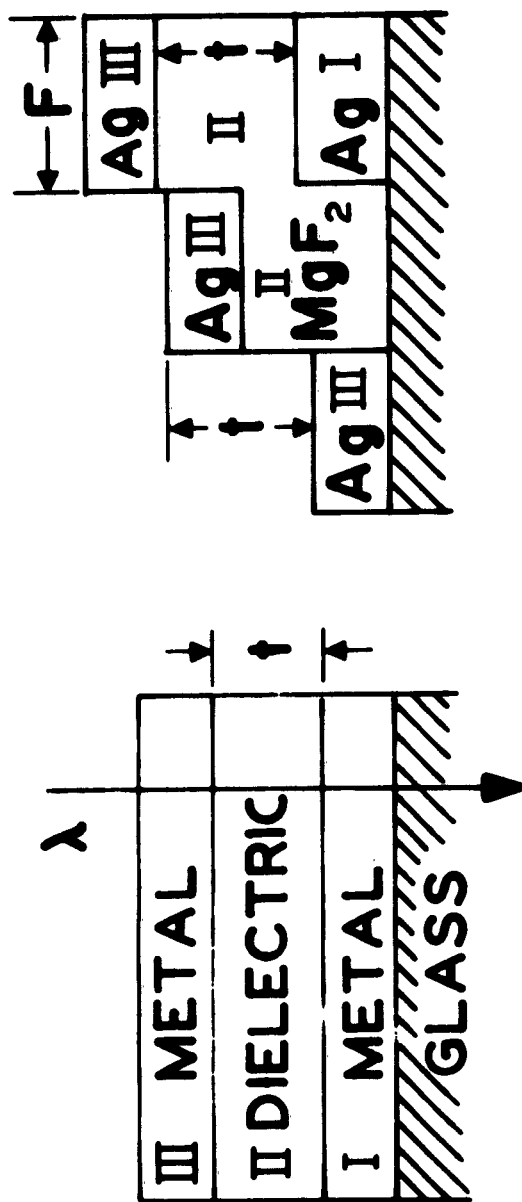
Figure 6. Reflectivities for Ag.

A few remarks concerning the results of Hagen and Rubens¹⁸ may be in order. Their measurements of 1903 have been quoted repeatedly in the past 50 years to support the contention that the classical skin effect theory can be used to account for the infrared properties of metals. It is now evident that the skin effect theory cannot be used, and, moreover, the experimental work was not accurate. It happens that there was agreement at 25 microns between experiment and theory, but the agreement is not significant because both are wrong. Actually, as the new measurements show, for a metal like Ag the inertial properties of electrons are already significant at 25 microns and therefore the Drude theory must be used.

IX. DETERMINATION OF k BY PHASE CHANGE MEASUREMENT (See Reference # 6, 7, and 8.)

The metal being studied was used as a reflecting element in an interference filter.¹⁹ In Fig. 7A are shown the essential parts of such a filter: Part I is a metal deposited from the vapor onto a glass substrate. It was of such thickness that roughly one percent of the visible radiation was transmitted. (For silver this is approximately 600Å.) The second deposit, II, was of a dielectric usually MgF_2 . Its thickness was determined by the exact nature of the experiment. Finally the upper part, III, was another deposit of metal, of the same thickness as I. A wavelength λ of light transmitted by a filter of this type is obtained with Eq. (16).

$$\frac{2 n_o t}{\lambda} + \frac{\psi}{\pi} = N \quad (16)$$



A.

B.



II AIR



C.

Figure 7. Filter Design.

Here n_0 is the index of refraction of the MgF_2 and t is thickness. The angle ψ is the phase change at the MgF_2 -Ag interface, and N is the interference order number. If t is sufficiently great, there will be several wavelengths $\lambda, \dots, \lambda_i$; which will be transmitted. A relation between these wavelengths is given in Eq. (17).

$$(N \lambda / n_0)_1 - \left(\frac{N \lambda}{n_0} \right)_1 = (\psi \lambda / n_0)_1 - (\psi \lambda / n_0)_1 \quad (17)$$

In Fig. 7B is shown the arrangement of a sample on which the measurements of the thickness t can be made, and also the wavelengths λ_i which are transmitted. The region labelled F is the filter while the step height "t" is a measure of the dielectric thickness. Methods²⁰ exist for measuring t , and the wavelengths were measured on a 21' grating spectrograph (manufactured by Jarrell Ash). The index of refraction n_0 of the dielectric was known from an earlier publication.⁵ The first metal to be studied in the visible region by this procedure was Ag. Extension of the range to 0.9μ was made with the type filter in Fig. 7C; Eq. (17) was used to find the values of ψ . In the wavelength region above 0.4μ the index of refraction n of Ag is so low that it can be neglected in Eq. 4 during the calculations to obtain k . The values of k thus obtained are given in Table II

Having once established the k values of Ag, a comparison method was used for other metals. Fig. 8A shows the principal parts of the transmission filters used for this purpose. On one side of a sheet of mica of uniform thickness a deposit of silver Ag' was laid down. Part of the opposite side was covered with silver Ag" and the

TABLE II. Values of the absorption coefficient k as a function of wavelength for Ag, Au, Cu, and Al.

(μ)	Ag	Au	Cu	Al
0.40	1.93	3.92
0.45	2.42	1.88	2.20	4.32
0.50	2.87	1.84	2.42	4.80
0.55	3.32	2.37	2.42	5.32
0.60	3.75	2.97	3.07	6.00
0.65	4.20	3.50	3.65	6.60
0.70	4.62	3.97	4.17	7.00
0.75	5.05	4.42	4.62	7.12
0.80	5.45	4.84	5.07	7.05
0.85	5.85	5.30	5.47	7.15
0.90	6.22	5.72	5.86	7.70
0.95	6.56	6.10	6.22	8.50

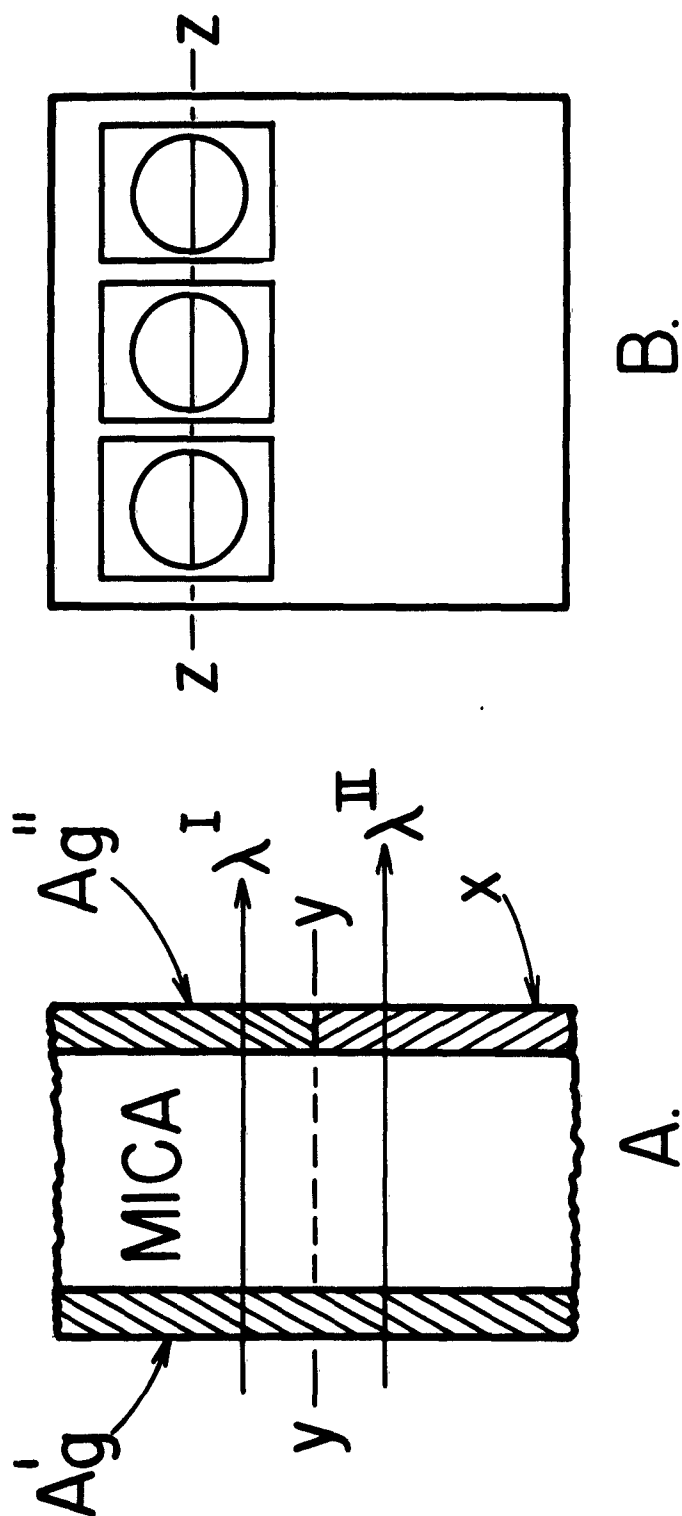


Figure 8. Mica Filter Design.

remainder with the metal x under investigation. There were then two filters: one with the sequence AG'-mica-Ag'', and a second with the sequence Ag''-mica-x. By measuring the difference in the wavelengths λ^I and λ^{II} it was possible to obtain the phase change associated with the mica-x interface. From this Ψ value it was possible to calculate k using Eq. (4). Values obtained for Au, Cu, and Al are given in Table II. Comparisons with earlier work showed good agreement for the case of Ag, but for Au, Cu, and Al the new values tended to be somewhat higher than the older ones.

X. TRANSMISSION EXPERIMENTS. (See Ref. # 10)

Transmission experiments are more difficult to do than reflection experiments because they require thickness measurements, but to compensate they usually yield more information. Also, values can be obtained which are characteristic of the bulk metal rather than the surface. Fig. 9 shows transmission as a function of thickness for several wavelengths. In contrast to materials other than metals, pure exponential absorption does not occur for these samples, but sets in only after about 400Å. Each curve of Fig. 9 has two features, a slope and an extrapolated intercept. Comparing the graph with Eq. (6), the slope is associated with the exponential and the intercept with the pre-exponential, C. Because of this behavior of metals one set of measurements yields two values of k: The first and more important is that found from the slope. It gives k_1 for the interior. In addition, the extrapolation to zero thickness leads to a second value of k, that is, k_s , for the surface. Because

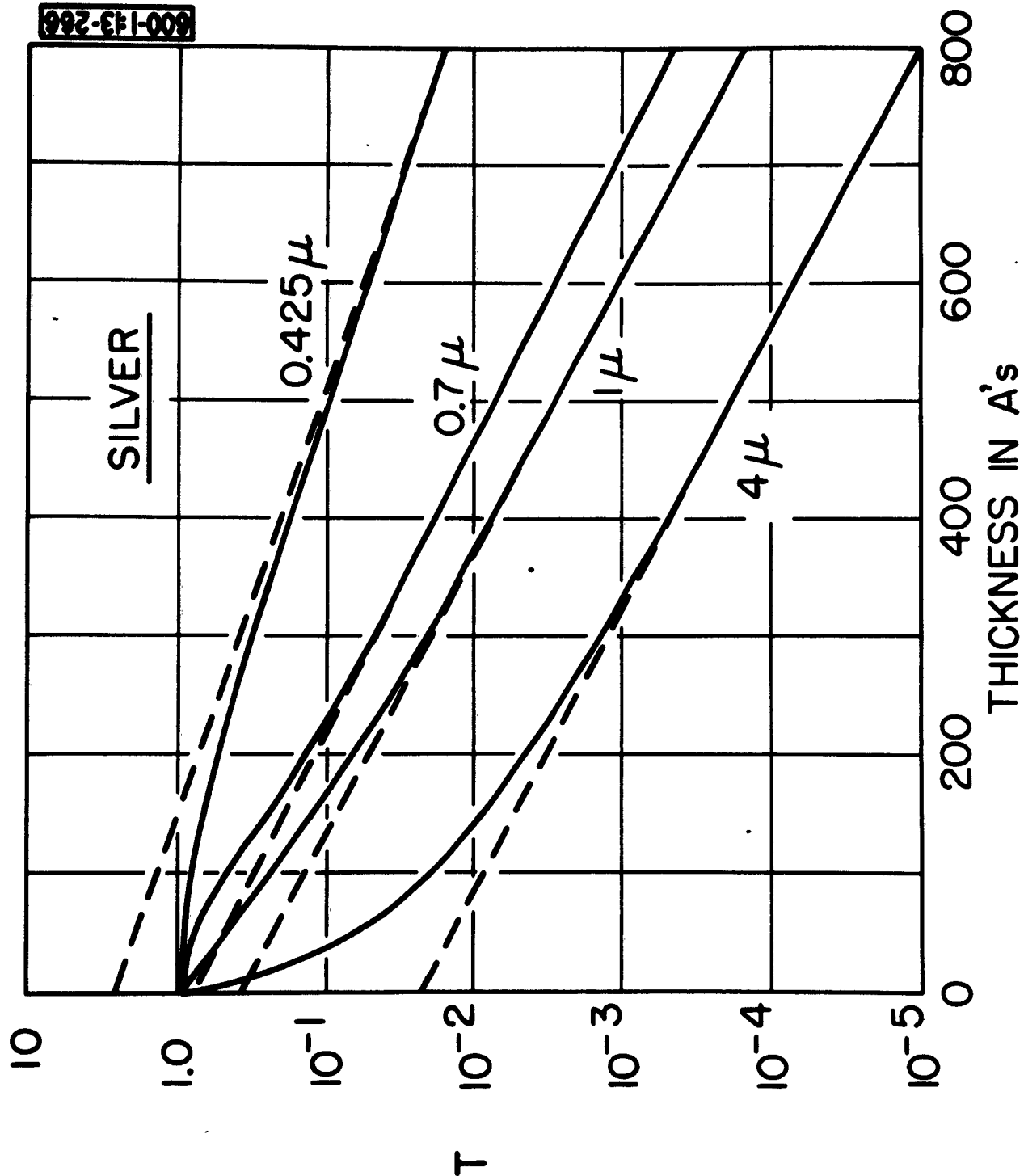


Figure 9. Transmission vs: Thickness of Ag.

of surface effects k_s should come out lower than k_i .

Samples were prepared by condensation from the vapor as shown in Fig. 10. Three thicknesses of the metal were deposited simultaneously onto a pair of quartz substrates, α and β . By means of a stepped rotor these were made in the exact ratio of 2:3:4. One component of the pair called beta was used for thickness determinations by an interference method. The other component, called alpha, was reserved for the transmission measurements.² These thicknesses were usually in the neighborhood of 300A, 450A, and 600A. Eq. (6) and (7) were used to calculate values for k_i and k_s .

Fig. 11 shows the general features of the results for Ag-significant numerical values are repeated in tables. First, concerning the code, the subscript i refers to the interior of a metal, and S to the surface. ST means a surface value obtained by a transmission experiment; SR means a surface value by reflection. Obviously, all surface values should be equal, whether by transmission or by reflection. Curves ABC are new experimental values, whereas Minor²¹ and FF²² refer to older measurements. Across the top the broken line labelled "Drude" is obtained by calculation.

The most general feature of the curves is their tendency to agree with, or approach the theoretical curve beyond 1 micron, but to depart drastically below 1 micron. The curve for the interior labelled A is slightly above the Drude curve. One of the surface values, given in B, is by transmission, and the other, C, is by reflection involving the phase change angle. In the wavelength region where B and C overlap they almost coincide.

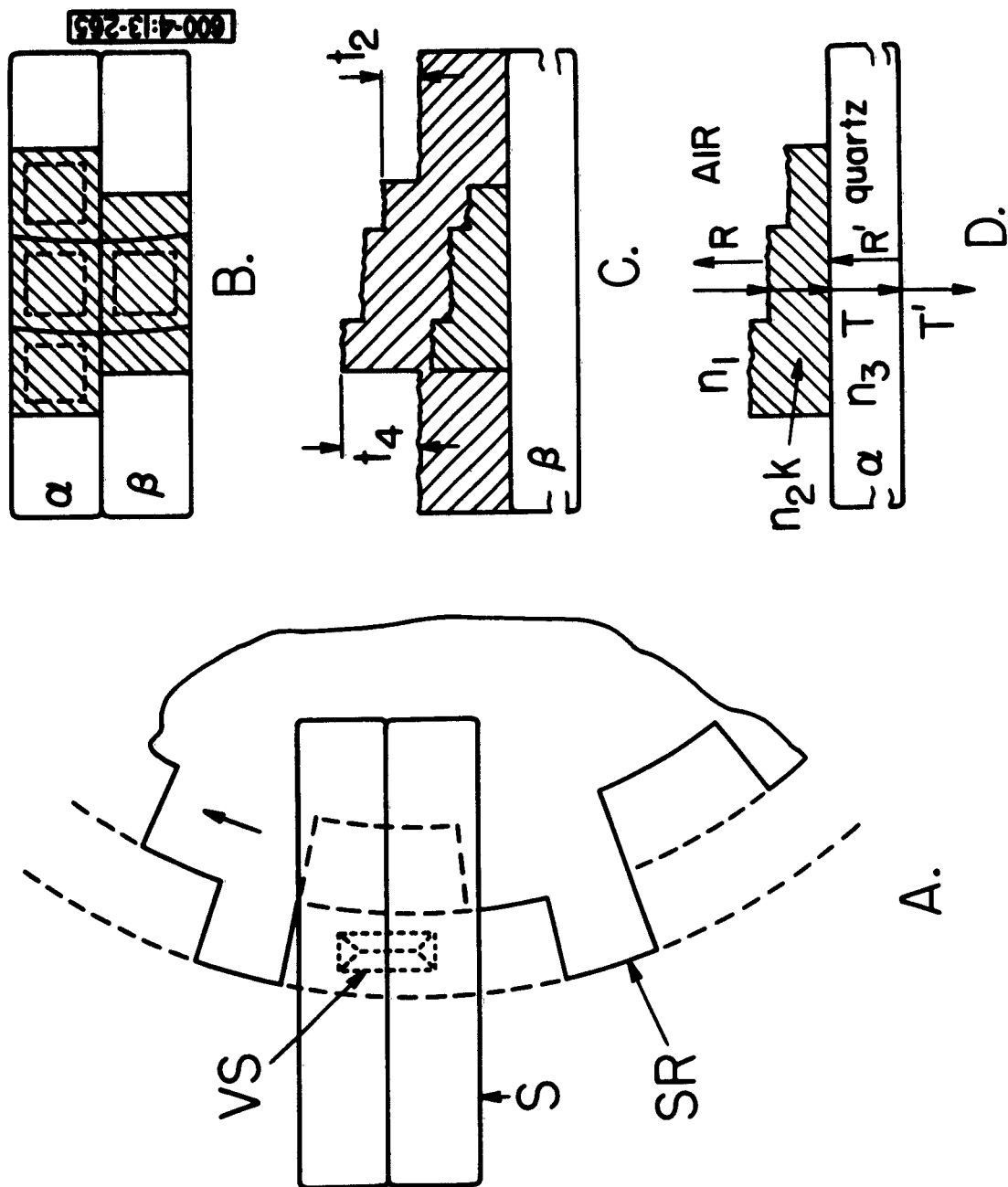


Figure 10. Construction of Transmission Filter.

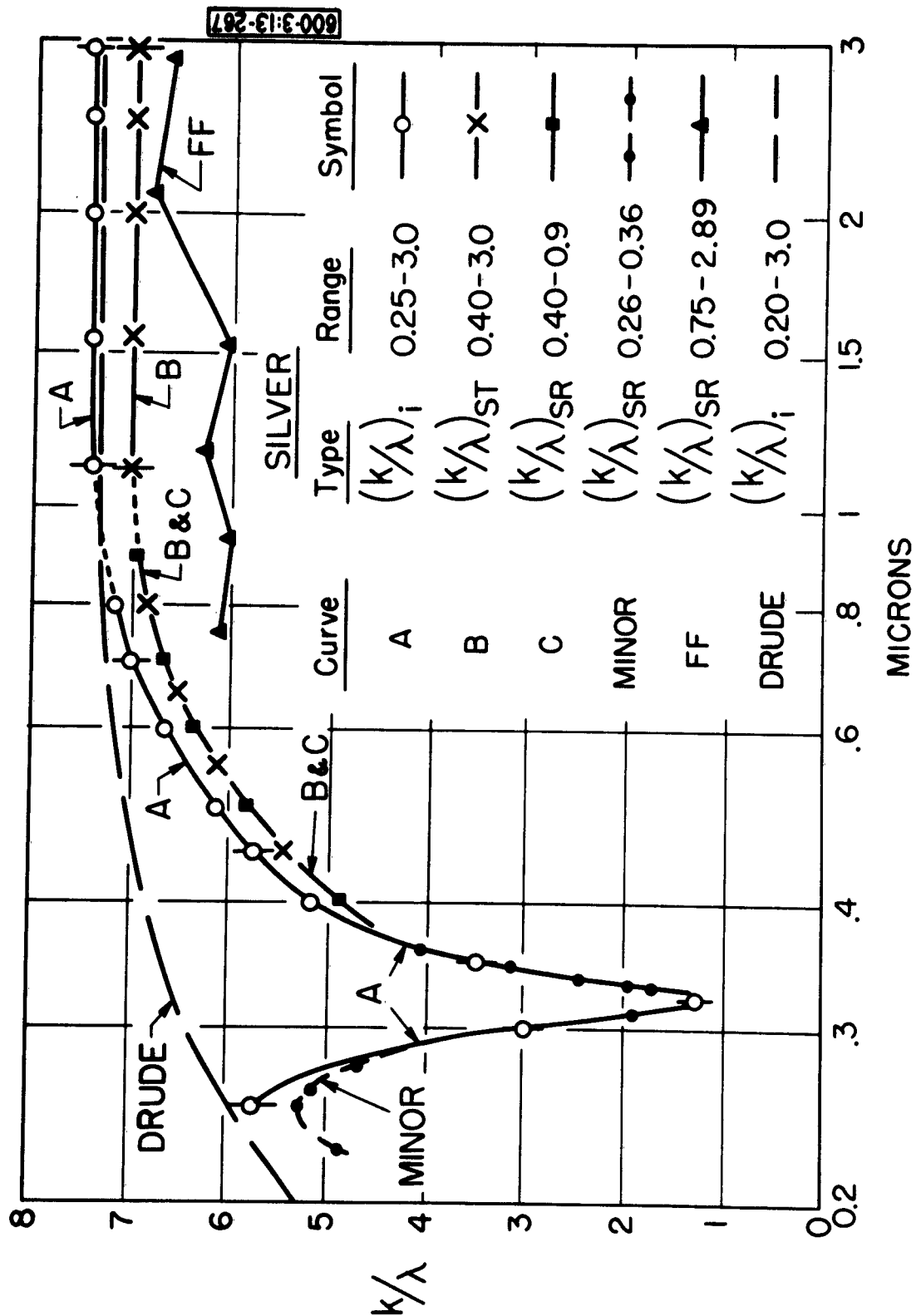


Figure 11. Various k/λ values for Ag.

This very large deviation from Drude at 3200A is due to a mechanism other than free electron absorption. Accordingly, the surface and bulk values should be identical here as is nicely shown by the experimental results.

Beyond 1 micron the difference between bulk and surface values is of the order of 6%. It is easier to get a good sample for transmission measurements, therefore curve A is likely to be dependable. Surface measurements leading to curve B were subject to much greater uncertainty. Actually, in the infrared region the difference of 6% is only a rough value.

These results for Cu shown in Fig. 12 are similar to those for Ag, with a few differences, however. Since the minimum occurs at a much larger wavelength, in fact in the middle of the visible, it is necessary to go to much larger wavelengths before k/λ levels off in the manner required by theory. Again at the minimum, surface and bulk values are the same. Below the minimum the new bulk value is decidedly higher than the older surface measurement. In fact so high that it is certain at least one of the curves is not correct. The most important result for Cu is the great deviation from the Drude theory. This dashed line is for an effective mass of $1.45 \times$ the free mass. It was chosen to bring about agreement at two microns. Au was also studied, but nothing new turned up.

Beyond two microns the curves for both Cu and Ag have leveled off. At this wavelength the Drude values of k/λ are those shown in the first column of Table III. Ag and Au are almost identical, but Cu is higher because of its smaller crystal constant. In the calculations m^* was taken equal to the free mass and the chemical valence

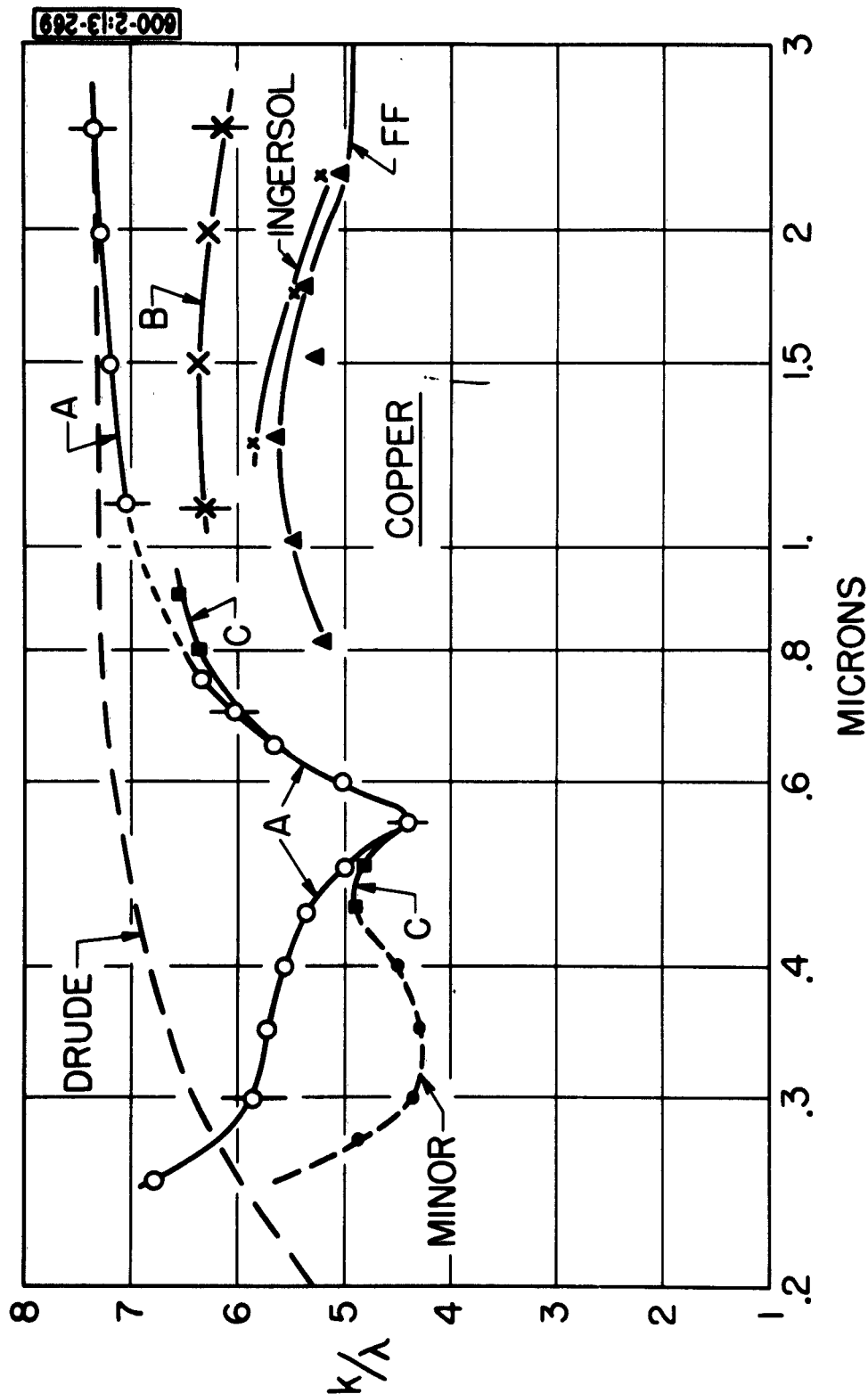


Figure 12. Various k/λ values for Cu.

TABLE III. k/λ Values at 2μ

Metal	Drude Eq.	Interim	Surface
Ag	7.29	7.45	7.00
Au	7.31	7.40	6.25
Cu	8.72	7.30	6.95

TABLE IV. Comparison of various m^*/m values.

Metal	Present investigation	FF	Electronic specific heat
Ag	0.97	1.07	1.18
Au	0.98	1.13	...
Cu	1.45	2.56	1.47

was used in determining the electron density. In the second column are the experimental values for the interior. They are approximately the same for all three metals. Finally, the last column gives the surface values. Each is about 6% lower than the corresponding bulk value.

The k/λ values beyond two microns for all three metals showed the required dependence, but not the proper absolute magnitudes. The calculated values could be brought into agreement with the experimental by assuming the values, shown in Table IV, for the ratio, m^* over m . For Ag and Au the difference from unity is about the experimental error. This result indicates that for these two metals the electrons are practically free. For copper, as has been mentioned, the rather high value of 1.45 is needed. In the second column are values from older optical experiments in 1913. In the last column are values from electron specific heat measurements.¹³ For Cu there is good agreement between the first and third column, but for Ag it is poor.

XI. CONCLUSION

Experimental work is still in progress, therefore it is impossible at this point to make a final statement concerning the value of optical methods for testing theories of metals. It does seem, however, that for "good" monovalent metals the original Drude theory is able to account for many of the observed optical properties. In a more general sense there may be reason to hope for something that might be called the absorption spectroscopy of metals.

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FIGURE LEGENDS

1. Graph showing the variation in reflectivities with changing angle of incidence for a particular set of values for k , n , and n_0 . Note that at 45° the value of R_s^2 is equal to R_p .
2. Sketch of the Electromagnetic Spectrum.
3. Graph for Ag showing the wavelength variation of n/λ and k/λ as found by calculation using the Drude theory. [Eqs. 12-14 of the text].
4. The Four Prism Samples Used for Measuring the Intensity of Reflection.
5. Values of the Index of Refraction n for Ag, Au, Cu and Al.
6. Graph showing the reflectivity R_0 at a metal-air interface for Ag as a function of wavelength. HR refers to reference 15.
7. Drawings which show schematically the sequence of deposits for various type filters. The thickness t of the dielectric was usually selected to keep the integer N of Eq. (16) equal to unity for all arrangements except C, where it varied from about 4 to 10.
8. Details of the filter construction and the arrangement for wavelength measurements. Drawing A shows how three such pairs were mounted over holes in a sheet of metal.
9. Transmission T versus thickness of Ag for several wavelengths. The broken lines are extensions of the linear portions of the curves; their intersections on the vertical axis (for zero thickness) define the C values. For zero thickness the transmission curves converge to near 0.97 which is the transmission of an air-quartz interface.
10. Drawings showing experimental details. In A the substrates S were placed as close as possible to the stepped rotor SR. The distance from the vapor source VS to the substrates was 25 cm. In B the shaded area is that over which metal was deposited; the dashed squares show the regions in which transmission was measured. In C and D the surface of the metal has been drawn rough to approximate the actual situation.

Figure Legends (Cont.)

11. Graph showing various k/λ values for Ag as a function of wavelength. Probable experimental errors are indicated by vertical lines.
12. Graph showing various k/λ values for Cu as a function of wavelength. The code for labeling is approximately the same as that for Fig. 11. In some cases the range is different as can be seen directly from the graph. In the calculations to obtain the curve labeled "Drude", m^* was taken equal to $1.45m$.